OIL IS ONE OUR MOST IMPORTANT energy sources [1], [2]. However, the wide use of oil could lead to diverse environmental problems, such as oily wastewater discharge. Oily wastewater is water that has become contaminated through oil and gas production, the refinery process, transportation, or storage. The dispersion and dissolution of oil fractions into water result in its contamination with free oil and grease, aliphatic hydrocarbons, aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes, known as *BTEX*), phenols, polycyclic aromatic hydrocarbons (PAHs), and highly soluble organic compounds (e.g., carboxyl acids) [3]–[5]. Many of these components are toxic, persistent, and bioaccumulative, posing a threat to ecosystems and human beings [6]–[9]. Thus, efficient treatment of oily wastewater is a necessity.

Many treatment technologies have been developed and applied to remove organic contents from oily wastewater. The traditional options include gravity separation, distillation, adsorption, coagulation, filtration, chemical oxidation, and biological degradation [3], [10]. Gravity separation can segregate dispersed oil but is incapable of removing higher soluble organics, such as phenols, PAHs, and carboxyl acids, among which PAHs are considered to be mutagens and carcinogens [11]. Other available technologies have shown many advantages in oil removal, but disadvantages were also observed (high operation and maintenance cost, long processing time, chemical input, and secondary pollution, among others). Therefore, greener and more effective technologies are greatly desired for treating oily wastewater.

Photooxidation has been widely applied in the removal of organic matter and has proved to be low in cost,

Oily Wastewater Treatment by Nano-TiO₂-Induced Photocatalysis

Seeking more efficient and feasible solutions.

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low in selectivity, and efficient in terms of completed mineralization [12]–[14]. Photocatalysis has the advantage of photooxidation, and its efficiency has been significantly accelerated by applying photoactive semiconductors [15], [16]. Among these, nano-scaled titanium dioxide (TiO_2) exhibits high stability, low cost, and low toxicity toward both humans and the environment. Thus, it has been extensively studied in treating a variety of municipal and industrial wastewater types [17]–[19]. Nano-scaled TiO_2 (such as nanoparticles, nanotubes, and nanofibers) shows great enhancement of photoactivity by providing a larger specific surface area compared with bulk TiO_2 [20]. Nano-scaled TiO_2-induced photocatalysis has been applied to remediate different types of onshore and offshore oily wastewater, targeting the individual compounds and/or all the organics [21]–[23].

To demonstrate the applicability of photocatalysis, an in-depth review of the mechanisms for removing organics from oily wastewater by photocatalysis is desired. Furthermore, the development of more efficient catalysts and a better understanding of the role of influencing factors are important. Thus, this review focuses on the application of nano-scaled TiO_2-induced photocatalysis in treating oily wastewater, including the effect of the water matrix, the influencing factors, and enhancement and development of the photocatalysis.

OVERVIEW OF OILY WASTEWATER TREATMENT

CHARACTERIZATION OF OILY WASTEWATER

Oily wastewater refers to any water containing oil from many industrial processes, such as oil and gas exploration, production, and transportation; petroleum refining; and onshore and offshore oil spills [2], [24], [25]. Concentrations of oil, the major contaminant in oily wastewater, vary widely among sources, ranging from 1 to 40,000 mg/L [2]. The effluents from oil and gas production and transportation are the largest waste streams of oily wastewater (e.g., produced water, bilge water, and refinery wastewater) [3]. The total oil and grease concentration of offshore produced water should be no higher than 42 mg/L based on existing regulations [24]. Not included are the soluble oil fractions, such as the carboxyl acids (0.001–10,000 mg/L), aliphatic hydrocarbons, BTEX (0.068–578 mg/L), PAHs (40–3,000 μg/L), and phenols (0.4–23 mg/L), which results in a concentration of total organic carbon (TOC) as high as 11,000 mg/L [3], [4]. Bilge water has a higher concentration of TOC (31–19,040 mg/L) and phenol (15–902 mg/L) than produced water [9]. Petroleum refinery effluent contains 20–4,000 mg/L of oil and grease, 200–600 mg/L chemical oxygen demand (COD), 20–200 mg/L phenol, and 1–100 mg/L benzene [26].

The toxicity of these chemical components in oily wastewater, especially petroleum hydrocarbons and phenol derivatives, has raised concerns over their effects on marine ecosystems and the environment in general [6], [27], [28]. The acute and chronic toxicity of PAHs and alkylated phenols has been well indicated [11]. It was also discovered that alkylphenols have a higher potential for bioaccumulation because of their high hydrophobicity and that they cause irreversible endocrine disruption in the sexual development of young fish [29]–[31]. Therefore, strict regulations have been established to control the emission of oil and grease in produced water (a 42 ppm daily maximum) [3], bilge water (15 ppmv) [32], and refinery effluent (a 7.5-lb per 1,000 barrels of crude oil daily maximum).

OILY WASTEWATER MANAGEMENT PRACTICE

To comply with the regulations, the oil and grease must be removed first. The main treatment technologies reported include gravity separation, hydrocyclone, sorption, chemical precipitation, flotation, membrane filtration, chemical oxidation, and biodegradation [5], [10], [24], [33], [34]. The most common and widest application is water/oil separation, which relies on gravity and density differences [3], [4]. To realize an effective water/oil separation, the most commonly used facility has been identified through the combination of a skim tank, a parallel plate separator, a hydrocyclone, and a flotation device [35]. However, water/oil separation cannot remove very small droplets and dissolved hydrocarbons [4]. To remove dissolved organic contaminants from wastewater, many available technologies have been used after the water/oil separation process, including coagulation, adsorption, membrane filtration, chemical oxidation, and activated sludge [2], [5], [26].

Coagulants added to oily wastewater can destabilize the oil emulsion, resulting in oil aggregation. Larger oil droplets can subsequently be removed by sedimentation or flotation [36]. Adsorption is effective in removing most oil and other organic materials but requires continuous regeneration and replacement. In addition, the adsorbed wastes
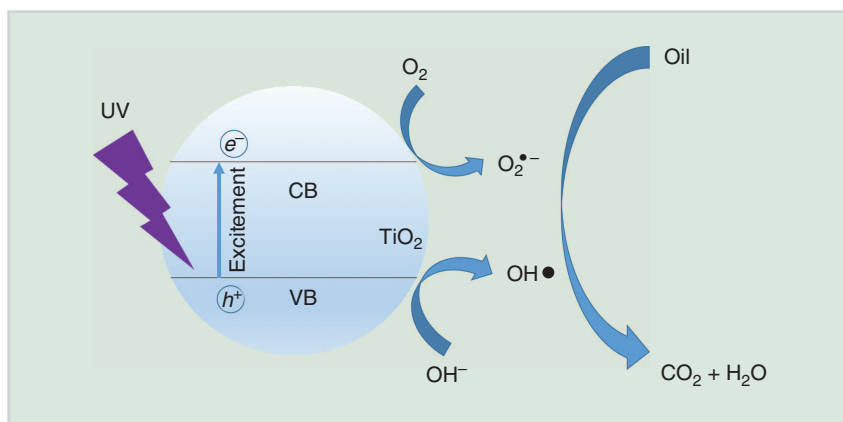
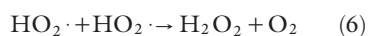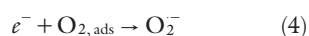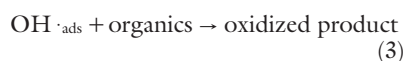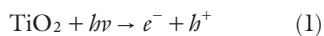**FIGURE 1** The mechanism of photocatalysis by a UV light source.

must be shipped to shore landfills, which increases the treatment cost. Membrane filtration technologies are able to remove small oil droplets and hydrocarbons larger than 0.005 μm [37], but fouling of the membranes is a major problem, and the technology is limited in oil field-type applications. Bioremediation has the capacity to remediate the organic matter in heavily loaded oily wastewater. However, this technology is time consuming, is inefficient in the degradation of aromatic organics, has a narrow range of appropriate reaction conditions (e.g., temperature and pH), and requires disposal of the spent, contaminated activated sludge [3], [26].

BASICS OF PHOTOCATALYSIS

Photocatalysis is an advanced oxidation process that has been extensively studied in remediating environmental samples contaminated by various organic pollutants [17], [38], [39]. The photocatalytic process, which has shown promise in terms of complete mineralization of organic pollutants, has strongly attracted scholars' attention. The photocatalytic degradation of aliphatics, aromatics, polymers, dyes, surfactants, pesticides, and so forth into carbon dioxide, water, and mineral acids can be achieved under mild conditions with no waste disposal. Photocatalysis is the acceleration of photolysis by adding photosensitive semiconductors. The most common semiconductors for photocatalysis include TiO_2, zinc oxide (ZnO), cadmium sulfide, gallium arsenide, gallium phosphide, and tungsten trioxide

[40]. Among these, TiO_2 has been discovered to be an ideal semiconductor for photocatalysis because of its high stability, low cost, and safety for both humans and the environment [13], [17].

The photocatalytic mechanism is initiated by the absorption of a photon with energy (hv) equal to or greater than the band gap of TiO_2, producing an electron–hole pair on the surface of the TiO_2. An electron is promoted to the conduction band (CB), while a positive hole is formed in the valence band (VB). Excited-state electrons and holes recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface (Figure 1). After reaction with water, these holes produce hydroxyl radicals with high redox oxidizing potential. Depending upon the exact conditions, the holes, OH radicals, O_2^-, H_2O_2, and O_2 play important roles in the photocatalytic mechanism [41] as follows:

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + OH_{ads}^- \rightarrow OH \cdot_{ads} \quad (2)$$

$$OH \cdot_{ads} + organics \rightarrow oxidized\ product \quad (3)$$

$$e^- + O_{2,ads} \rightarrow O_2^- \quad (4)$$

$$O_2^- + H^+ \rightarrow HO_2 \cdot \quad (5)$$

$$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2 \quad (6)$$

$$H_2O_2 + e^- \rightarrow OH \cdot_{ads} + OH^-. \quad (7)$$

TiO_2 polymorphs in nature include anatase (tetragonal), brookite (orthorhombic), and rutile (tetragonal), each

with different optical properties [42]. The band gaps of anatase, rutile, and brookite are 3.2, 3.02, and 2.96 eV, respectively [43], resulting in absorbable wavelengths of light irradiation that should be shorter than 400 nm. In other words, only ultraviolet (UV) and near-UV light have the capacity to excite TiO_2. The anatase structure has the highest band gap, and it is preferred over other polymorphs for photocatalysis applications because of the higher electron mobility, low dielectric constant, and lower density [40] compared with rutile, which tends to recombine electrons and holes, preventing the transport of electrons.

Various investigators have reported that TiO_2 is more effective in the form of nanoparticles than as bulk powder [42]. When the crystallite diameter falls below a critical radius of about 10 nm, the band gap increases, and the band edges yield a larger redox potential [41]. The higher redox potential provides a stronger driving force, increases the rate constant of the charge transfer (the rate-limiting step in photocatalysis), and then increases the photoactivity of the nanoparticles. Additionally, the smaller size of the TiO_2 allows a higher chance of mass transfer because of a larger surface area, thus increasing the photoactivity.

APPLICATION OF PHOTOCATALYSIS TO OILY WASTEWATER

Many attempts have been made to apply photocatalysis in treating oily wastewater and are summarized in Table 1. Most of the studies applied TiO_2 and UV and/or solar light to degrade the oil contents in different types of wastewater and showed good results [44]–[47]. The water types can be classified as artificial wastewater and authentic wastewater. The artificial wastewater samples were prepared by spiking distilled water and/or seawater with the target pollutant [48]–[50]. The authentic wastewater samples were prepared by either contaminating the water samples with crude oil [51] or diesel [52] or were obtained from already contaminated sources [7], [53], [54]. The target pollutants, such as oil [55], COD [56], dissolved organic carbon (DOC) [57],

TABLE 1 A summary of photocatalysis for different types of oily wastewater.

WASTEWATER TYPE	CATALYST	TREATMENT PROCESS	TARGET POLLUTANT	MAJOR FINDINGS	REACTION RATE CONSTANT	REFERENCE
ARTIFICIAL WATER	Nano-TiO$_2$–SiO$_2$	Fixed-bed system plus sunlight	Naphthenic acid	92% removal after 4 h		[48]
	Nano-TiO$_2$	1,000-W xenon lamp	Naphthalene, Dibenzothiophene, p-Nitrophenol		0.032~0.052/min^{-1} 0.009~0.019/min^{-1} 0.009~0.068/min^{-1}	[49]
	Nano-TiO$_2$ coated on quartz sand	20-W UV lamp, 254 nm	Phenol	50~100% in 6 h, depending on the initial concentration		[50]
ARTIFICIAL WATER AND SEAWATER	Nitrogen-doped TiO$_2$ nanotube	6-W black-light lamp and 20-W tungsten lamp	MB, toluene, and 1-hexadecene	Toluene 26% with N-TNT and 14% with TNT; Less than 10% with visible light; 1-hexadecene: 10% degradation under UV light source	0.38 mg toluene/g N-TNT/h 0.25 mg 1-hexadecene/g N-TNT h	[60]
	Degussa P25, Aerosil T805	1,500-W xenon lamp with 340 nm ~79 mW	Toluene Dodecane		2.7×10^{-2}~15 7.7×10^{-4}~0.82	[63]
BILGE WATER	K-TiO$_2$	UV lamp with light intensity of 49 W/m^{-2}	COD	100% oil decompostion in 2 h		[44]
	K-TiO$_2$	Ultrafiltration and UV lamp with light intensity of 49 W/m^{-2}	Oil and COD	Filtration: 96~98% removal; photocatalysis: 100% removal in 2 h		[64]
	TiO$_2$ PC500	Air stripping plus 125-W UV lamp 365 nm	Oil	60% removal in 8.5 h	0.009×[HC]	[32]
CRUDE OIL AND CONTAMINATED WATER	Nano-TiO$_2$ loaded on ceramic microbeads	Near-UV solar irradiation, 25~50 W/m^{-2}	PAHs	100% removal		[59]
	Degussa P25	150-W Hg lamp plus H$_2$O$_2$	TOC	>50% TOC removal after 10 h		[65]
	Exfoliated graphite/ZnO composites	UV irradiation 20 W/m^2	Oil	Sorption: 50~57 g/g, 85% removal after 160 h of irradiations		[66]
	Degussa P25, P25 supported on NaY zeolite	125-W high-pressure mercury arc for 100 h	Linear alkane, branched alkane, cyclic alkane, and aromatic compounds	Linear alkanes 98.66%, branched alkanes 97.31%, cyclic alkanes 96.04%, aromatic compounds 99.54%; with zeolite: linear alkanes 79.85%, branched alkanes 45.38%, cyclic alkanes 58.10%, aromatic compounds 91.85%		[45]
	TiO$_2$ nanotube and modified TiO$_2$ with stearic acid	Irradiated with a lamp of 765 W/m^2 and 300–800 nm	Alkane, PAHs	Alkane ineffective	PAH removal: 0.08~0.14/h	[8]
CRUDE OIL CONTAMINATED SEAWATER	Nano-TiO$_2$	Photocatalysis followed by biofilm	Oil	90% of oil removal	0.027/min^{-1}	[46]
	Degussa P25	125-W Hg lamp 366 nm	Water-soluble fraction	100% removal after 1–2 d		[67]
	Degussa P25	25-W Hg lamp 366 nm	DOC	Adsorption: 25% in the first 12 h Photocatalysis: 90% after 7 d		[51]
DIESEL IN SEAWATER	Nano-ZnO	UV irradiation	Diesel	84% removal in 3 h		[52]

(continued)

TABLE 1 A summary of photocatalysis for different types of oily wastewater. *(Continued)*

WASTEWATER TYPE	CATALYST	TREATMENT PROCESS	TARGET POLLUTANT	MAJOR FINDINGS	REACTION RATE CONSTANT	REFERENCE
DIESEL IN WATER	Polyurethane foams modified with silver/titanium dioxide/graphene ternary nanoparticles (PU-Ag/P25/G)	UV irradiation	Diesel	Adsorption 96 g/g; degradation 76% in 16 h		[23]
	Bi/N-doped TiO_2 on expanded graphite C/C (EGC) composite	500-W xenon lamp with UV cutoff filters	Diesel		$0.0029–0.0062/min^{-1}$ depending on the Bi load	[68]
GROUND WATER CONTAMINATED BY GASOLINE AND DIESEL	TiO_2–SiO_2 solution dip-coated on ceramic beads.	Irradiated by sunlight (1.6 mW/cm^2 measured at 365 nm) with H_2O_2	TPHs, BTEX, TOC	>70% degradation of BTEX and TPH		[58]
OFFSHORE-PRODUCED WATER	Degussa P25 and Immobilized TiO_2 on glass plate	8-W UV lamp	Naphthalene		Dispersion $0.00219/min^{-1}$ fixed plate; $0.00305/min^{-1}$	[53]
	TiO_2	8-W UV lamp	PAHs	>50% PAHs removal in 24 h	$>0.0005/min^{-1}$	[69]
	Immobilized TiO_2 on glass plate	8-W UV lamp plus Ozone	PAHs	>90% removal in 1 h	$0.05–0.29/min^{-1}$	[70]
OIL SANDS PROCESS-AFFECTED WATER	Degussa P25	Natural sunlight 25 J/m^2	Acid-extractable organics TOC	>90% removal over 14 d; 45% TOC removal		[7]
OIL SLICK ON WATER	Degussa P25 on floating substrate	420 W/cm^{-2} at 330~430 nm plus O_2	Toluene 1-Decene	100% degradation in 45 min 30% removal in 2 h		[71]
OIL SLUDGE	Degussa P25	373 μW/cm^{-2} at the wavelength range from 290 to 390 nm and 10.4 μW/cm^{-2} at 254 nm with H_2O_2	PAHs TOCs	PAHs removal 100% after 96 h TOC removal 80%		[47]
PETROLEUM REFINERY SOURWATER	Degussa P25	250-W UV light	DOC	DOC removal 21% within 1 h		[54]
PRODUCED WATER	Fe-doped TiO_2	N/A	Oil and COD	Oil removal 89.1% COD removal 98.5%		[56]
REFINERY WASTEWATER	Nano-TiO_2 loaded on Fe-ZSM-5	8-W UV lamp	COD	Photocatalytic removal 61.35%, adsorption removal 4% in 3 h		[72]
	Nano-TiO_2	Irradiated with UV lamp with 520 MW/cm^2	COD	70% removal in 2 h		[22]
	ZnO, P25, and TiO_2	Irradiated with 108 W/m^2 at 254 nm plus H_2O_2	Phenol DOC	Phenol removal 93% DOC removal 56% in 1 h		[57]
	Nano-TiO_2	Irradiated with UV lamp with 520 MW/cm^2	COD	COD removal 83% in 2 h	$0.007–0.013/min^{-1}$	[26]
WASTEWATER FROM POLYMER FLOODING	Nano-TiO_2	125-W Hg lamp	PAM	80% removal in 1.5 h		[62]
WEATHERED OIL AND CONTAMINATED WATER	Food-grade TiO_2 and Degussa P25	Irradiated by UV lamp (350–400 nm at 18 W/m^{-2})	Soluble organic carbon bioavailability	Soluble organic carbon conetent increased by 60% after 24 h Bioavailability enhanced by 37%		[55]

total petroleum hydrocarbon (TPH) [58], BTEX [59], phenols [26], PAHs [8], aliphatic carbons [60], organic acids [61], and polymers (e.g., polyacrylamide [PAM]) [62], cover the major hazardous organic compounds found in oily wastewater.

INFLUENCING FACTORS IN OILY WASTEWATER

High organic load, high salinity, and various impurities compose a complex matrix in oily wastewater. It significantly deteriorates the performance of adsorption and photocatalysis [21]. Catalyst surface charge could be vulnerable to the complex inorganic and organic composition of oily wastewater, which can result in reactivity reduction [69], [73]. The high concentration of organic substrates can saturate the TiO_2 surface, reducing the photonic reactivity of the catalyst [17].

SALINITY

The presence of inhibitory ions of magnesium (Mg^{2+}), calcium (Ca^{2+}), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}), among others, can significantly reduce the effectiveness of the catalyst, especially for suspended nanoparticles, by blocking the active sites and/or forcing the agglomeration of the catalyst [74], [75]. Hsu et al. [60] indicated that the tendency toward agglomeration (particle–particle interaction) also increases at high solid concentration, resulting in a reduction of the surface area available for light absorption. The adsorption competition between cationic ions and diesel on the catalyst surface becomes significant in relatively high salinity [68]. The competing ions might occupy the active sites, thus decreasing the photocatalytic efficiency against the diesel. The higher concentration of anions further changes the catalyst surface, altering its point of zero charge and thus changing the electrostatic interaction with the organics [76]. The presence of halides could significantly affect photocatalysis by scavenging stronger radicals (e.g., hydroxyl radicals) to weaker halide radicals [69]. The radicals involved in the photocatalytic degradation process could further alter the breakdown pathways of organics and potentially form toxic chlorinated by-products, which have been observed in the photocatalysis of saline waters [7], [77].

ORGANIC COMPOSITION

The composition of oily wastewater can significantly affect the efficiency of photocatalysis. Each organic species in oily wastewater responds differently to photocatalysis. Liu et al. [69] investigated the change in the organic composition of offshore produced water during photocatalysis. The findings suggested that organics with aromatic rings (PAHs and phenols) are more degradable, while alkanes are insensitive to photocatalysis within 24 h. This is probably because aromatic organics are much more vulnerable to photolysis [8], [14], whereas alkanes show negligible changes. The overall removal rates from oily wastewater could reach more than 90% after prolonged irradiation (100 h) [45]. Aromatic compounds still have the highest rate of degradation, and the breakdown rate of alkanes follow the rule of n-alkanes > branched alkanes > cyclic alkanes.

The effectiveness of photocatalysis is also affected by the organic load. When the organic load is less, photon flux and the activated catalyst site are sufficient for photodegradation. In this case, an organic load increase will increase the degradation rate [78]. At higher concentrations, however, the photon flux and activated site are insufficient for treating organics. The reaction rate remains constant or decreases. Therefore, the removal rate of organics will be decreased with an increase in the organic load. The increase in the organic load can further hinder reaction rates by 1) reducing the concentration of hydroxyl radicals through a higher consumption rate, 2) screening light through the increase of photosensitive organics, 3) accumulating organics on the catalyst because the adsorption rate is higher than the degradation rate, and 4) generating more adsorptive intermediates that occupy the activated sites on the catalyst [14], [78], [79].

The additives in oily wastewater could enhance or hinder photocatalysis. Zhang et al. [68] evaluated the photocatalysis of diesel solutions with different concentrations of surfactants. It was indicated that a lower surfactant concentration could promote the diesel degradation by increasing its solubility. However, with a surfactant concentration higher than the critical micelle concentration, negative effects, such as photoattenuation and active site blockage of overdose, decrease the photodegradation of diesel.

INTERMEDIATE

The goal of photocatalysis is mineralization. Nevertheless, the intermediates generated from incomplete mineralization are inevitable in treating oily wastewater because of the high organic load. Leshuk et al. [7] observed that over 90% of acid-extractable organics were phototransformed after a one-day irradiation, but that only 45% of the TOC was removed. This suggested that the acid-extractable organics were transformed to oxidized intermediates instead of being completely mineralized. Ziolli and Jardim [67] analyzed the composition change of the soluble oil fraction in oil-contaminated marine waters during the heterogeneous photocatalysis process, finding 63 new peaks on the gas chromatograph. These peaks represented oxidized intermediates that contain oxygen atoms, with most having lost their aromatic character during irradiation. They further suggested that these compounds might actually be more toxic to marine organisms than the originals.

> The intermediates generated from incomplete mineralization are inevitable in treating oily wastewater because of the high organic load.

> The pH controls the surface charge of the catalyst, the reduction potential of hydroxyl species, and the affinity of the pollutant for the catalyst surface.

Hashimoto et al. [80] characterized the by-production during photocatalysis of different organic species. For aliphatic hydrocarbons, the common intermediates are oxidized to alcohols, aldehydes, and carboxylic acids, while phenol, catechol, hydroquinone, and muconic acid are detected in the degradation of benzene. It should be noticed that hydroquinone and benzoquinone are considered to be scavengers for oxidative radicals [7], so further photocatalytic oxidation is dramatically inhibited. Zulfakar et al. [50] observed that the formation of intermediates also significantly affects the rate of reaction by competing on the active sites. Fouling of the catalyst surface can also occur through the polymerization of PAHs during the photocatalytic process [8].

CONFIGURABLE FACTORS IN THE PHOTOCATALYTIC PROCESS

To remediate the deterioration of the water matrix through photocatalysis, the optimization of configurable factors, such as light sources, catalyst concentration, surface area, temperature, pH, and oxidant concentration (e.g., O_2 and H_2O_2), is important.

LIGHT SOURCES

The light intensity among the studies varies from milliwatts per square centimeter [8] to microwatts per square centimeter [47] with an energy consumption of 8–1,500 W [53], [63]. Light intensity and wavelength directly affect the reaction rate. Da Rocha et al. [47] applied two lights of the same wattage but different light intensity and wavelength in treating oil sludge. The black-light mercury lamp emitted 98 lx and 373 $\mu W/cm^2$ at a wavelength range from 290 to 390 nm and 10.4 $\mu W/cm^2$ at 254 nm, while the white light was 1,900 lx and 74 $\mu W/cm^2$ at a wavelength range from 290 to 390 nm and 11.2 $\mu W/cm^2$ at 254 nm. The results showed that white light with a higher light intensity has a higher TOC removal rate. Furthermore, compared with another study [8], the complete degradation of PAHs under 76.5 mW/cm^2 was much accelerated, from four days to several hours, indicating that the higher light intensity resulted in a higher degradation rate.

Han et al. [81] applied two UV lamps (185 nm and 254 nm) with TiO_2 toward decomposition of *p*-chlorobenzoic acid and figured out that the rate constants for TiO_2 at 185 nm were 3.0–6.5 times as much as those for TiO_2 at 254 nm. Photocatalysis with natural sunlight attracts many researchers because of the free light source. Berry [71] evaluated the photocatalytic degradation of toluene and 1-decene with different light sources: a UV lamp and sunlight. The results showed that the degradation rate of toluene with $UV/TiO_2/O_2$ is only slightly higher than that with sunlight/TiO_2/O_2, suggesting that the UV light intensity from the sun might be sufficient. Leshuk et al. [7] indicated a complete degradation of acid-extractable organics in oil sands process-affected water achieved by solar photocatalysis in 1–7 d. Cho et al. [58] proved that more than 70% of BTEX and TPH in gasoline/diesel-contaminated groundwater can be degraded by the solar light/TiO_2 slurry system. It should be noted that most of lamps with high energy consumption were simulating solar light. This energy efficiency is much lower than the UV lamp, as only UV light and near-UV light have wavelengths lower than 400 nm.

CATALYST

Karakulski et al. [64] indicated the optimal catalyst content to be in the range of 0.8–1.2 g/L in treating the oil in ultrafiltration permeate. King et al. [8] applied a high dose (3% and 9%) of TiO_2 nanotubes on an oil slick and showed that the best dose of TiO_2 nanotube was 9%, by which a 93% enhancement in the observed degradation rate constant of very small PAHs (one to two rings) was reached compared with no oxide irradiation. The degradation of larger PAHs was not well accelerated or even inhibited. They further indicated that TiO_2 addition could increase light attenuation, thus inhibiting the photolysis of PAHs, especially large PAHs, which are the most photoactive. Saien and Neiati [22] observed that the photocatalytic degradation rate increases with the increase of suspended catalyst concentrations, up to about 100 mg/L. Greater than that concentration results in a turbidity increase and a reduction of light transmission, consequently decreasing degradation.

Shahrezaei et al. [26] found that a maximum reduction in COD was achieved with a catalyst concentration of 100 mg/L. They further pointed out that the agglomeration of the catalyst in high doses could reduce the surface area for light absorption and hence decrease the degradation rate. Santos et al. [57] tested TiO_2 particles of different sizes: TiO_2 (Brunauer–Emmett–Teller [BET] surface areas of 1.7 and 8.3 m^2/g) and Degussa P25 (a 30-nm particle size and a 50 ± 15-m^2/g BET surface area) in the photodegradation of phenols in petroleum wastewater samples. The results showed that P25 in lower doses has a great enhancement (five times) in phenol removal, implying that a larger surface area can significantly enhance photocatalysis.

pH

The pH controls the surface charge of the catalyst, the reduction potential of hydroxyl species, and the affinity of the pollutant for the catalyst surface [26], [82]. The pH could further enhance or hinder the photodegradation efficiency by controlling the electrostatic interaction between the catalyst surface, organic molecules, and generated radicals [72]. Saien

and Neiati [22] analyzed the removal of organic pollutants in petroleum refinery wastewater (PRW) at different pHs. When the pH was lower than the pH of the zero point of charge (pH_{zpc}), the positive charge of the catalyst would attract more anions, thus increasing the removal rate. Similar results can be found in Shahrezaei et al. [26]. Most of the organic matter in PRW consists of phenol and phenolic derivatives. These are negatively charged after ionization, and their electrostatic attraction to the TiO_2 surface is favorable at a low pH, where the TiO_2 was positively charged.

Santos et al. [57] pointed out that the best pH for degrading the majority of wastewater organic pollutants (alkanes), which are nonpolar, is pH_{zpc}, where the TiO_2 surface is neutral. Ginemo et al. [83] investigated the adsorption of fluorene on TiO_2 at pH = 2 and pH = 5. Higher pH resulted in higher adsorption and consequently a higher degradation rate. Vargas and Nunez [49] conducted photocatalytic degradation of several representative compounds at different pHs. The results indicated that the degradation rates were dibenzothiophene > naphthalene > p-nitrophenol at pH = 3. Both naphthalene and p-nitrophenol have higher degradation rates at a basic pH (e.g., 10). Generally, there can be higher concentrations of hydroxyl radicals in water with a basic pH, but Zhang et al. [68] indicated that the agglomeration of catalytic particles could accelerate in an overly acidic or overly alkaline solution and finally reduce the surface area. To achieve better efficiency, they found, the pH should be kept neutral, which allows better particle dispersion and formation of hydroxyl radicals.

TEMPERATURE

The influence of temperature has been studied by many researchers. Saien and Neiati [22] observed the positive influence of temperature during the photocatalysis of PRW. They further pointed out that photocatalytic degradation is usually accelerated by increased temperature because of the increase of TiO_2 electron transfer. Gahsemi et al. [72] evaluated the interaction between catalyst dose and temperature. The outcome indicated that

the efficiency increased as temperature increased when the optimal dose of catalyst had been selected. Leshuk et al. [61] observed the neglected effect of temperature on degrading naphthenic acids in oil sands process-affected water. They stated that the increase of temperature might increase catalyst aggregation, thus mitigating the overall reaction rate.

OXIDANT

Oxidants have a vital role in the reaction, as they absorb the free electrons on the catalyst surface, produce the hydroxyl radicals, and dramatically accelerate the reaction rate. O_2 and H_2O_2 are often chosen to enhance photocatalysis [71], [77], [84]. Berry and Mueller [71] aerated the photocatalytic system with O_2, by which the degradation rate of toluene was significantly improved and that of 1-decene was slightly increased. Cazoir [32] summarized two important roles that oxygen plays in photocatalysis: 1) it prevents the electron–hole recombination by scavenging the photogenerated electron, and 2) it reacts with other species (O_2, OH^-) and produces reactive oxygen species, such as O_2^- and $HO_2\cdot$, which improve the oxidation efficiency.

The addition of H_2O_2 produces increased degradation in two ways [77]: 1) it reacts directly with organics and easily decomposes to OH radicals, and 2) it provides a more active electron acceptor compared with O_2. Pernyeszi and Dekany [65] applied H_2O_2 in the photocatalytic oxidation of a crude oil emulsion. The results showed that the TOC removal rate was increased from 20% to 50%. Cho et al. [58] added 10-mM H_2O_2, which significantly increased the degradation

efficiency in both the slurry and immobilized systems. With an optimal dose of H_2O_2 (4~10 mM), COD removal from oilfield-produced wastewater was enhanced 3.5 times [77]. Santo et. al [57], by contrast, observed no significant changes after adding H_2O_2 to the continuous-aeration system, implying that the bubbling provides sufficient oxidant. Therefore, the addition of oxidant and the dose should be specific to different types of oily wastewater.

ENHANCEMENT OF NANO-TiO$_2$-BASED CATALYSTS

Photocatalysis shows strong potential for treating oily wastewater. However, the application of the technology is restricted by the low reaction rates for some organic species, insufficient mass and photon contact rates for catalysts under high organic loads, and the sophisticated recovery process. Therefore, modification of the catalyst to achieve a wider range of light absorbance, higher photon–electron conversion rate, and more feasible application are much desired.

DOPING OF NANO-SCALED TiO$_2$

The band gaps of TiO_2 are more than 3.0 eV, so only UV light can induce the catalyst, which means that most sunlight energy is wasted. To extend the application of TiO_2 more widely, the technology of doping other materials to the TiO_2 surface has been studied [23], [42], [85]. Doped TiO_2 introduces intraband-gap states, decreasing the band gap, and it can be induced by lower-energy photons (Figure 2).

Transition metal ions provide additional energy levels within the band gap
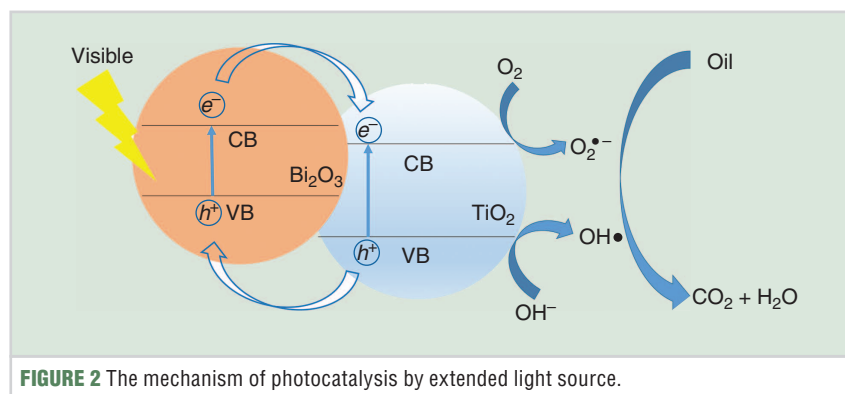

FIGURE 2 The mechanism of photocatalysis by extended light source.

> The combination of photocatalyst and adsorbent has been studied in treating oily wastewater to enhance catalysis effectiveness.

of a semiconductor; electrons can transfer from one of these levels to the CB through photons of lower energy [86]. Noble metals can obtain the electron from TiO_2, as the hole remains on the TiO_2. This reduces the electron–hole recombination possibility, which increases the efficiency of the photoinduction [42]. Nonmetallic or anionic elements, such as carbon, sulfur, halides, phosphorus, and boron seem to have more significant advances: it unlikely form recombination center but reduce the band gap that improve the photocatalytic activity [60], [87]. Zhang et al. [68] doped both bismuth (Bi) and nitrogen (N) with nano-TiO_2 and examined its photocatalytic efficiency under a visible light source. $Bi_{1.0}$–N–TiO_2/expanded graphite carbon/carbon composite (EGC) showed excellent performance in mineralizing diesels, proving the extended capacity of doped TiO_2 applied under solar light. It further indicated that the presence of a lower concentration of Bi on TiO_2 intensified the absorption of visible light and reduced the electron–hole recombination rate, while higher percentages resulted in the reduction of photon excitement.

IMMOBILIZATION OF NANO-SCALED TiO_2

Immobilization of nano-scaled TiO_2 is still limited to industrial applications because of the inconvenient catalyst-recovering step of suspended TiO_2 from the treated water at the end of the operation. Membrane filtration, microfiltration, and ultrafiltration may be able to remove fine particles, but the drawbacks are significant: higher transmembrane pressure, higher fouling potential, and greater flux declination [53]. Therefore, to increase the efficiency and longevity of nano-scaled TiO_2 and prevent the inconvenient catalyst-recovering step after treatment,

many studies focus on immobilization of nano-scaled TiO_2. It has been proven that TiO_2 immobilization has advantages in terms of catalyst recovery and ease of handling, but the surface area becomes much lower than that of suspended TiO_2, and the mass transfer rate is limited [88]. The approach of synthesizing nano-scaled TiO_2 with different structures (nanofiber, nanowire, nanorods, and so on) increases the size of the bulk TiO_2 without compromising the reduction in surface area. Another solution to increasing the catalyst area is coating TiO_2 on different substrates with a relatively large surface area, such as quartz sand [50], microbeads [59], glass fiber [89], membranes [90], carbon nanotubes [91], and absorbents [45], [92].

Liu et al. [53] compared the photodegradation of PAHs in offshore produced water by TiO_2 powder and immobilized TiO_2. The effectiveness of photocatalysis was slightly higher with the immobilized catalyst, indicating that the immobilization is more resistant to the water matrix. Cho et al. [58] indicated that the addition of H_2O_2 could enhance the efficiency of immobilized TiO_2 and narrow its difference with that of TiO_2 slurry. Wang et al. [62] added a mixture of TiO_2 and surfactant in treating oily wastewater to trap the TiO_2 particles in the interface. Heller et al. [93] attached TiO_2 on ceramic microbeads maintained at the air–oil interface. These microbeads with catalyst can deploy into the environment and allow a long-term catalytic photolysis of spilled oil, which has potential in arctic applications.

MODIFICATION OF THE ADSORBENT SURFACE WITH NANO-SCALED TiO_2

The combination of photocatalyst and adsorbent has been studied in treat-

ing oily wastewater to enhance catalysis effectiveness [66]. Composite TiO_2 on the surface of an adsorbent combines the advantages of both: 1) large-surface-area adsorbents work as the support for nano-sized TiO_2 and concentrate the pollutants and intermediates around the TiO_2, 2) nano-sized TiO_2 photocatalysts can decompose the pollutants, thus regenerating the adsorbent in situ, and 3) a TiO_2/adsorbent composite can capture photodecomposed intermediates, preventing possible secondary pollution [94].

Ghasemi et al. [72] coated TiO_2 onto Fe-ZSM-5 and applied it to the treatment of refinery wastewater. The coating of TiO_2 resulted in the reduction of the specific surface area, but the highest photocatalytic activity was achieved compared with a simple mix of zeolite and Degussa P25. However, the addition of an adsorbent could have a negative effect. D'Auria [45] observed that a TiO_2/zeolite composite could reduce the overall degradation rate of the organic species in crude oil because of light scattering. Zhang et al. [68] used expanded graphite as an adsorbent because of its extraordinary oil adsorption rate. It was indicated that in combination with the catalyst, the specific surface area was enlarged. The adsorbent not only shortened the distance between the organic and photocatalytic sites but played a role as a floating substrate to keep the catalyst between the air–liquid interface. The adsorbent, with a similar function, has also been used to treat diesel [23]. The catalyst with graphene significantly enhanced the adsorption effect to 96 g of diesel per gram of catalyst. It should be considered, however, that the overwhelming effect of adsorption could inhibit the photocatalytic process because of a reduction of the mass transfer rate inside the adsorbent. Therefore, the balance between photocatalysis and adsorption should be carefully evaluated.

SYSTEM DESIGN

The effectiveness of photocatalysis depends critically on both the mass and photon contact rates of the catalyst. To optimize the photocatalytic effectiveness, various processes have been proposed

aimed at increasing the contact efficacy and contact time. An annular photoreactor can shorten the photon travel path [95]. With tangential inlet and outlet tubes, an annular reactor increases the mixing rate within the system [96]. Laoufi et al. [97] used a helical photoreactor to maximize the irradiation time. Yu et al. [98] coated a helical support with TiO_2 and combined it with an annular reactor to increase the contact time of pollutants and photons with the TiO_2 layer. A fixed-bed system with an immobilized catalyst has shown advantages in terms of having no need of downstream separation processing and allowing continuous-flow treatment [99].

Combination with other technologies can also increase the applicability of photocatalysis. Karakulski et al. [64] first filtered bilge water using ultrafiltration. The filtration process removed 96–98% of the oil, which is more than 350 mg/L. The complete decomposition of oil in the ultrafiltration permeate was achieved after 2 h of UV illumination using a potassium $(K)/TiO_2$ photocatalyst. Photocatalysis has the capacity to treat organics with high toxicity and low biodegradability. Residual organic carbon was found to be significantly more biodegradable than the initial acid-extractable organics [7]. Therefore, photocatalysis followed by bioremediation could significantly reduce the overall intention time [46]. The combination of photocatalysis with ozone is very effective in promptly degrading organics such as phenol in a short period (5 min) [84]. It increases the biodegradation rate of treated water from 13% to 40%.

REGENERATION

The lifetime of a photocatalyst is an important parameter for evaluating its feasibility in real applications. The deactivation of a catalyst during photocatalytic degradation can significantly increase the operational cost because of the frequent changes of catalyst that are needed. Leshuk [7] reused the catalyst and observed some loss in five treatment cycles (~20% lower apparent rate constant). The process of centrifugation and resuspension increases the

aggregation of the particles and thus reduces the specific surface area. They suggested that the deactivation of the photocatalyst could be mitigated by better dispersion or particle-washing techniques. Ghasemi et al. [72] reused the TiO_2/Fe-ZSM-5 nanocomposite three times. A slightly decreasing trend of the COD removal rate was observed. The accumulated organic substrate and intermediates blocked the activated site of the catalyst.

To reactivate the catalyst, several approaches have been made. The organic fouling of the catalyst can be treated by calcination, burning out the organics and keeping the catalyst stable and reusable [72]. However, this technology consumes additional energy. Zhu and Zou [100] applied different technologies (e.g., UV, UV plus H_2O_2, and UV/ultrasound) to regenerate the used photocatalyst and found that the combination of ultrasound and UV has the shortest process time. They further indicated that the ultrasound could 1) generate hydroxyl radicals that oxidize the fouling organic on the catalyst surface and 2) produce ultrasonic waves to break the aggregation of catalyst particles into a smaller size and mechanically clean their surface.

SUMMARY

This article summarized various kinds of photocatalytic applications in oily wastewater treatment. Nano-TiO_2-induced photocatalysis is a promising technology in treating petroleum hydrocarbons that has proven to be very attractive because of its higher mineralization, lesser selectivity, and lower toxicity. However, the lower efficiency and mineralization rate caused by the complex matrix of oily wastewater, the higher energy consumption, and sophisticated posttreatment could hinder the application of the technology.

Greater effectiveness with lower cost is the major goal of technology adaptation. The approaches to this are system configuration and catalyst modification. The use of solar light with doped TiO_2 can replace UV light, which has a much higher energy consumption. Light-emitting diode light can also be an option

because of its higher electron–photon conversion rate. Immobilizing TiO_2 on a larger, porous structure or on a fixed surface allows for continuous treatment of oily wastewater without subsequent separation. In combination with an adsorptive substrate, the concentrate-and-treat approach allows for continuous treatment of the oil fraction for remediating oil spills. These approaches are therefore more functional and do not greatly compromise degradation efficiency.

The research on photocatalysis applications to oily wastewater is still in an early stage. To increase applicability, more effective catalysts with greater durability are desired. Further research is also needed for application in larger-scale systems. In-depth and systematic studies on the interaction of the water matrix and surface change during photocatalysis as well as studies on the more generalized system simulation and optimization are required to maximize removal efficiencies and predict reaction performance globally.

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